

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB05/000279

International filing date: 26 January 2005 (26.01.2005)

Document type: Certified copy of priority document

Document details: Country/Office: GB
Number: 0401644.0
Filing date: 26 January 2004 (26.01.2004)

Date of receipt at the International Bureau: 25 February 2005 (25.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



Put GB2905/000279



INVESTOR IN PEOPLE

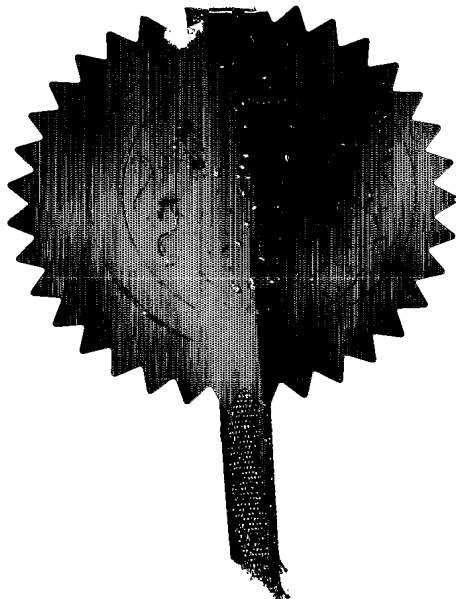
The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

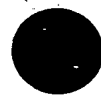
In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed *Stephen Hordley*

Dated 11 February 2005



11



27JAN04 E868328-1 D00571
P01/7700 0.00-0401644.0 NONE

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

26 JAN 2004

LONDON

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

PJS/ALH/P9727GB

0401644.0

2. Patent application number

(The Patent Office will fill this part in)

26 JAN 2004

3. Full name, address and postcode of the or of each applicant (underline all surnames)

CAMBRIDGE UNIVERSITY TECHNICAL SERVICES
LIMITED
16 Mill Lane
Cambridge CB2 1SB

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

7882871004

4. Title of the invention

METHOD OF PRODUCING CARBON-ENCAPSULATED
METAL NANOPARTICLES

5. Name of your agent (if you have one)

W. H. Beck, Greener & Co.

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

W. H. Beck, Greener & Co.
7 Stone Buildings
Lincoln's Inn
London WC2A 3SZ

Patents ADP number (if you know it)

323001

6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. Divisionals, etc: Complete this section only if this application is a divisional application or resulted from an entitlement dispute (see note f)

Number of earlier UK application

Date of filing
(day / month / year)

8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request?

Answer YES if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

Yes

Otherwise answer NO (See note d)

9. Accompanying documents: A patent application must include a description of the invention. Not counting duplicates, please enter the number of pages of each item accompanying this form:

Continuation sheets of this form

Description	10
Claim(s)	2
Abstract	0
Drawing(s)	7 + 7 <i>ll</i>

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for a preliminary examination and search (Patents Form 9/77)

Request for a substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature(s)

Beck, Green

Date 26.01.04

12. Name, daytime telephone number and e-mail address, if any, of person to contact in the United Kingdom

Mrs. Anna L. Hatt - (020) 7693 5600

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered YES in part 8, a Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- Part 7 should only be completed when a divisional application is being made under section 15(4), or when an application is being made under section 8(3), 12(6) or 37(4) following an entitlement dispute. By completing part 7 you are requesting that this application takes the same filing date as an earlier UK application. If you want the new application to have the same priority date(s) as the earlier UK application, you should also complete part 6 with the priority details.

METHOD OF PRODUCING CARBON-ENCAPSULATED METAL NANOPARTICLES

The present invention relates to a method of producing carbon-encapsulated metal nanoparticles.

5 Carbon-encapsulated magnetic nanoparticles are important new nanomaterials (Peter J. Harris, Chapter 5, "Carbon Nanotubes and Related Structures", Cambridge University Press, 1999). The carbon-encapsulated magnetic nanoparticles consist of magnetic nanoparticles (for example
10 of iron, nickel or cobalt) encapsulated within carbon nanotubes or fullerene-like or polyhedral graphitic cages. In either case, a completely sealed carbon structure is typically found. The typical particle size is 10 to 500 nm.

Applications of carbon-encapsulated magnetic
15 nanoparticles include high-density magnetic data storage, magnetic toners for use in photocopiers, magnetic inks and ferrofluids (S. Subramoney, Adv. Mater. 10, 1557, 1998). The carbon coatings mean that the magnetic nanoparticles are biocompatible and are stable in many organic media. Thus,
20 carbon-encapsulated magnetic nanoparticles are candidates for bioengineering applications, for example drug delivery, biosensors, magnetic hyperthermia and magnetic contrast agents for Magnetic Resonance Imaging (A. A. Bogdanov, C. Martin, R. Weissleder, T. J. Brady, Biochim. Biophys. Acta,
25 1193, 212, 1994).

Because of the protective graphitic sheets encapsulating the magnetic nanoparticles, the magnetic nanoparticles are protected from the environment and from degradation. In addition, the graphitic sheets isolate the
30 magnetic nanoparticles magnetically from one another. This means that problems caused by interaction between closely spaced magnetic bits are avoided.

Carbon-encapsulated magnetic nanoparticles have been produced by arc evaporation in the Huffman-Kratschmer chamber (T. Hayashi, S. Hirono, M. Tomita, S. Umemura, Nature, 381, 772, 1996; J. Henry, J. Scott and S. A.

5 Majetich, Phys. Rev. B, 52, No. 17, 12564, 1995). This technique involves evaporation of a mixture of metal catalyst and graphite by electrical arc discharge (typically 100 - 200 A) at extremely high temperatures (above 3000 °C).

Laser ablation has also been used. This method
10 produces carbon-encapsulated magnetic nanoparticles in a much higher yield than arc discharge. However, although both methods can produce good quality products, they are unsuitable for use on a large scale because of poor and irreproducible yields and presence of many carbonaceous by-
15 products.

Carbon-encapsulated magnetic nanoparticles have been produced by Chemical Vapour Deposition (CVD) by passing a carbon source (typically a hydrocarbon) over a supported metal catalyst. This method is low-cost and only requires
20 simple apparatus, and can be well controlled. However, this method cannot be used to produce carbon-encapsulated magnetic nanoparticles on a large scale because of poor yields and the difficulty of separating the carbon-encapsulated magnetic nanoparticles from the supporting
25 materials (Z. Y. Zhong, H. Y. Chen, S. B. Tang, J. Ding, J. Y. Lin, K. L. Tan, Chem. Phys. Lett., 330, 47, 2000).

Carbon-encapsulated magnetic nanoparticles have also been produced by pyrolysis of non-graphitising carbon (P. J. F. Harris and S. C. Tsang, Chem. Phys. Lett., 293, 53,
30 1998). The non-graphitising carbon is first impregnated with a salt of the metal to be encapsulated. The dried product is heated to temperatures of 1800 to 2500 °C. The

encapsulated products are similar to those prepared by the arc discharge method. However, the yield of product is low.

The present inventors have invented a new method suitable for large scale synthesis of carbon-encapsulated magnetic nanoparticles.

Accordingly, in a first aspect, the present invention provides a method of producing carbon-encapsulated metal nanoparticles, comprising the steps of:

providing a carbon-containing metal salt or organometallic compound in a reactor; and decomposing the carbon-containing metal salt or organometallic compound to form carbon-encapsulated metal nanoparticles.

Preferably, carbon is maintained within the reactor during decomposition. The carbon may be in elemental or molecular form. Carbon should be maintained at a vapour pressure at the reaction site adequate to ensure that carbon-encapsulated metal nanoparticles are formed. It is not necessary for all carbon contained in the metal salt or organometallic compound to be maintained within the reactor.

Preferably, decomposition is carried out in a reactor having a restricted opening. The reactor thus substantially confines the carbon within the reactor where it reacts to form carbon-encapsulated metal nanoparticles. It is preferred to provide a restricted opening so that by-products of decomposition can escape from the reactor.

Preferably, the reactor is a tube having one sealed end and one end with a restricted opening. The tube should have a large length to diameter ratio, for example a ratio of 30 or higher. This also assists in confining carbon within the reactor. Alternatively, the reactor may be a flask having a restricted opening.

Preferably, a means of escape for elements other than carbon and metal released during decomposition (e.g. oxygen and nitrogen) is provided. Suitably, a gas flow to carry away such elements is provided.

5 However, a unidirectional gas flow across the reaction site is preferably prevented. This assists in preventing carbon from being carried away from the reaction site. Where a flow of gas is provided during reaction, the flow should be directed towards the restricted opening of the
10 reactor.

Preferably, the carbon-containing metal salt is decomposed under an inert gas atmosphere. This prevents formation of metal oxides and carbon dioxide. Preferably, a flow of inert gas is provided.

15 Suitably, the inert gas is argon. If nitrogen is used as an inert gas, some incorporation of nitrogen into the product may be found.

Preferably, the carbon-containing metal salt is decomposed by heating. Alternatively, the salt may be
20 decomposed by irradiation.

Preferably, heating is carried out at a temperature of 700 to 1500 °C. More preferably, heating is carried out at a temperature of 700 to 1200 °C. A temperature below 700 °C favours the formation of amorphous carbon. A temperature
25 above 1500 °C leads to rapid decomposition which may result in agglomeration of the metal to form large chunks. Such chunks are not normally catalytically active.

Preferably, the metal is iron, nickel, cobalt, ruthenium, osmium, rhodium, iridium, palladium, platinum, a lanthanide
30 or uranium. More preferably, the metal is a magnetic metal.

Preferably, the carbon-containing metal salt or organometallic compound contains at least 5 carbon atoms per metal atom.

5 Preferably, the carbon-containing metal salt is a carboxylic acid metal salt. Suitably, the carbon-containing metal salt is a stearate.

In a second aspect, the present invention relates to carbon-encapsulated metal nanoparticles produced by a method as described above.

10

The invention will be further described with reference to the Examples and as illustrated in the Figures, in which:

15 Fig. 1 shows a TEM image of an encapsulated nanoparticle produced in Example 1.

Fig. 2 shows an SEM image of the carbon nanotubes produced in Example 1.

20 Fig. 3 shows a TEM image of two carbon nanotubes produced in Example 1.

Fig. 4 shows an X-ray diffraction profile of the product of Example 1.

25

Fig. 5 shows an SEM image of encapsulated iron nanoparticles produced in Example 4.

30 Fig. 6 shows a TEM image of an encapsulated Fe_3C nanoparticle produced in Example 4.

Fig. 7 shows X-ray diffraction and Raman spectra of the product of Example 4.

Example 1

5

Nickel stearate (about 1.5 g, fine green powder) was evenly distributed in a quartz reactor having the shape of a tube of length 500 mm and diameter 11 mm with a first sealed end and a second end with a small opening of diameter 4 mm.

10 The reactor was pumped to vacuum and filled with argon. The reactor was slowly introduced into a tubular furnace of length 800 mm and diameter 40 mm. The furnace was preheated to 800 °C and a flow of argon (1 to 2 l/min) was passed through the furnace. The small opening of the reactor was
15 directed towards the flow of argon. The reactor was heated in the furnace for 10 mins and the furnace was then cooled to room temperature. The produced was collected at room temperature.

During loading of the reactor into the furnace the
20 nickel stearate changed from green to black in colour. Some gas passed out of the reactor during heating. The product (a fine black powder) was examined by SEM and TEM and was found to consist of carbon nanotubes and carbon-encapsulated nickel nanoparticles in fullerene-like or polyhedral
25 graphite cages.

The carbon encapsulated nickel nanoparticles (Fig. 1) were found to have a typical diameter of 30 to 150 nm. The graphite layers were well crystallised with 10 to 50 layers.

The carbon nanotubes (Fig. 2) were found to have a
30 typical internal diameter of 10 to 30 nm, although some much finer tubes of diameter less than 5 nm and larger tubes of diameter larger than 50 nm were also observed. TEM

observations (Fig. 3) indicated that most nanotubes were multi-walled with 10 or more graphene layers. Many nanotubes also had nickel nanoparticles encapsulated inside.

5 No naked nickel nanoparticles were observed under intensive and repeated microscope observations, indicating that substantially all the nickel nanoparticles produced were encapsulated either in the fullerene-like or polyhedral graphitic cages or in carbon nanotubes. The yield of encapsulated nickel product was thus approximately 100 %.

10 Electron diffraction and X-ray tests (Fig. 4) confirmed that the encapsulated nickel nanoparticles were pure nickel nanocrystals and that the surrounding carbon was well crystallined graphite.

15 Elemental analysis indicated C: 74 % (corresponding to Ni: 26 %).

Example 2

The method of Example 1 was repeated at 1000 °C. 20 Examination of the products by electron microscopy indicated that they were similar in structure to the products of Example 1, but that the graphite layers were even better crystallined. This indicates further that a higher temperature increases the degree of graphitisation.

25

Example 3

The stability of the products of Example 1 was tested by heating a sample in air to 400 °C in a quartz vial and 30 cooling it to room temperature over 12 hours. No weight loss or colour change was observed. This indicates that the products had good thermal stability and that there was no

amorphous carbon in the products, since this would have burnt at a temperature of 355 to 400 °C to give a weight loss of the sample. It also indicates that there were no naked nickel particles in the sample since these would have
5 been oxidised. The good stability is also confirmed that no degradation has so far been observed for product exposed to air for over 10 months.

Example 4

10

The method of Example 1 was repeated using iron stearate rather than nickel stearate. The iron stearate was ground using a pestle and mortar. It was found that only carbon-encapsulated iron nanoparticles were produced (Figs.
15 5 and 6). No naked iron nanoparticles were produced. The product contained a small proportion of carbon nanotubes (estimated by SEM as less than 1 %).

X-ray examination (Fig. 7) indicated that the encapsulated species were pure iron nanocrystals and iron
20 carbide (Fe_3C) nanocrystals. The yield of encapsulated product was thus approximately 100 %.

Example 5

25 The method of Example 1 was repeated using cobalt citrate rather than nickel stearate. The product was a mixture of carbon-encapsulated cobalt nanoparticles and naked cobalt particles.

30 Comparative Example 1

Nickel stearate was heated to 800 °C in a boat under argon atmosphere. Naked nickel particles were produced.

Comparative Example 2

5

Example 1 was repeated using a reactor having the shape of a tube of length 500 mm and diameter 11 mm with both ends open. Naked nickel particles were produced.

10

The high yields of encapsulated product achieved in the Examples mean that these methods are suitable for bulk synthesis of carbon-encapsulated magnetic nanoparticles and carbon nanotubes.

15

The method of the Examples does not produce naked metal nanoparticles which are typical by-products in arc discharge. Further, the temperatures used in the Examples are much lower than those required for arc discharge. The apparatus used in the Examples is also much simpler than the arc discharge chamber.

20

The method of the Examples gives a much higher yield than the non-graphitising carbon method. Again, the temperatures used in the Examples are much lower than those required for the non-graphitising carbon method.

25

The method of the Examples does not require the separate carbon source, catalyst and supporting materials of the CVD method. Instead, the stearate salt provides these three functions.

30

Comparison of the Examples and Comparative Examples show that to achieve good results argon must not be allowed to flow freely over the metal salt. It is believed that confinement of atomic carbon near the reaction zone is

necessary for formation of the desired product. Use of a long tubular reactor also assists in confining carbon. The reactor used in the Examples has a length to diameter ratio of about 46.

5 Whilst the applicants do not wish to be bound by this theory, they believe that the large carbon to metal ratio of nickel stearate contributes to the good results achieved in the Examples.

10 In nickel stearate, the metal content is 9.4 wt% and the carbon content is 66 wt%. The metal content falls within the typical metal loading range for heterogeneous catalysts (5 to 10 %). In contrast to a heterogeneous catalyst, nickel stearate provides a medium in which the dispersion of nickel atoms is uniform at a molecular level.

15 Although the apparent ratio of carbon to nickel is 36 to 1, the inventors believe that the effective ratio is much higher. This is because as nickel atoms are formed by thermal decomposition of the salt they readily agglomerate to give particles, and only the nickel atoms on the particle surface are catalytically active. For example, a spherical
20 nickel particle with a diameter of 20 nm contains about 6.4×10^5 atoms of which only about 3.7 % are on the surface. This increases the effective carbon to nickel ratio to about 1000 to 1. The ratio increases as the particle size
25 increases.

30 The inventors believe that the high ratio of carbon to nickel within nickel stearate means that under appropriate conditions thermal decomposition of the molecule will produce nickel nanoparticles as catalytic seed and sufficient carbon atoms to provide feedstock for the growth of carbon nanostructures.

Claims

1. A method of producing carbon-encapsulated metal nanoparticles, comprising the steps of:
5 providing a carbon-containing metal salt or organometallic compound in a reactor; and decomposing the carbon-containing metal salt or organometallic compound whilst maintaining carbon within the reactor to form carbon-encapsulated metal
10 nanoparticles.
2. A method as claimed in Claim 1, wherein the reactor is a vessel having a restricted opening.
- 15 3. A method as claimed in Claim 2, wherein the vessel is a tube having one sealed end and one end with a restricted opening.
4. A method as claimed in any one of the preceding claims,
20 wherein a unidirectional gas flow across the reaction site is prevented.
5. A method as claimed in any one of the preceding claims,
25 wherein the carbon-containing metal salt or organometallic compound is decomposed under an inert gas atmosphere.
6. A method as claimed in Claim 5, wherein the inert gas
30 is argon.

7. A method as claimed in any one of the preceding claims,
wherein the carbon-containing metal salt is decomposed
by heating.
- 5 8. A method as claimed in Claim 7, wherein heating is
carried out at a temperature of 700 to 1500 °C.
9. A method as claimed in any one of the preceding claims,
wherein the metal is iron, nickel, cobalt, ruthenium,
10 osmium, rhodium, iridium, palladium, platinum, a
lanthanide or uranium.
10. A method as claimed in Claim 9, wherein the metal
is a magnetic metal.
- 15 11. A method as claimed in any one of the preceding
claims, wherein the carbon-containing metal salt or
organometallic compound contains at least 5 carbon
atoms per metal atom.
- 20 12. A method as claimed in any one of the preceding
claims, wherein the carbon-containing metal salt is a
carboxylic acid metal salt.
- 25 13. A method as claimed in Claim 12, wherein the
carbon-containing metal salt is a stearate or a
citrate.
14. Carbon-encapsulated metal nanoparticles produced
30 by a method as claimed in any one of the preceding
claims.

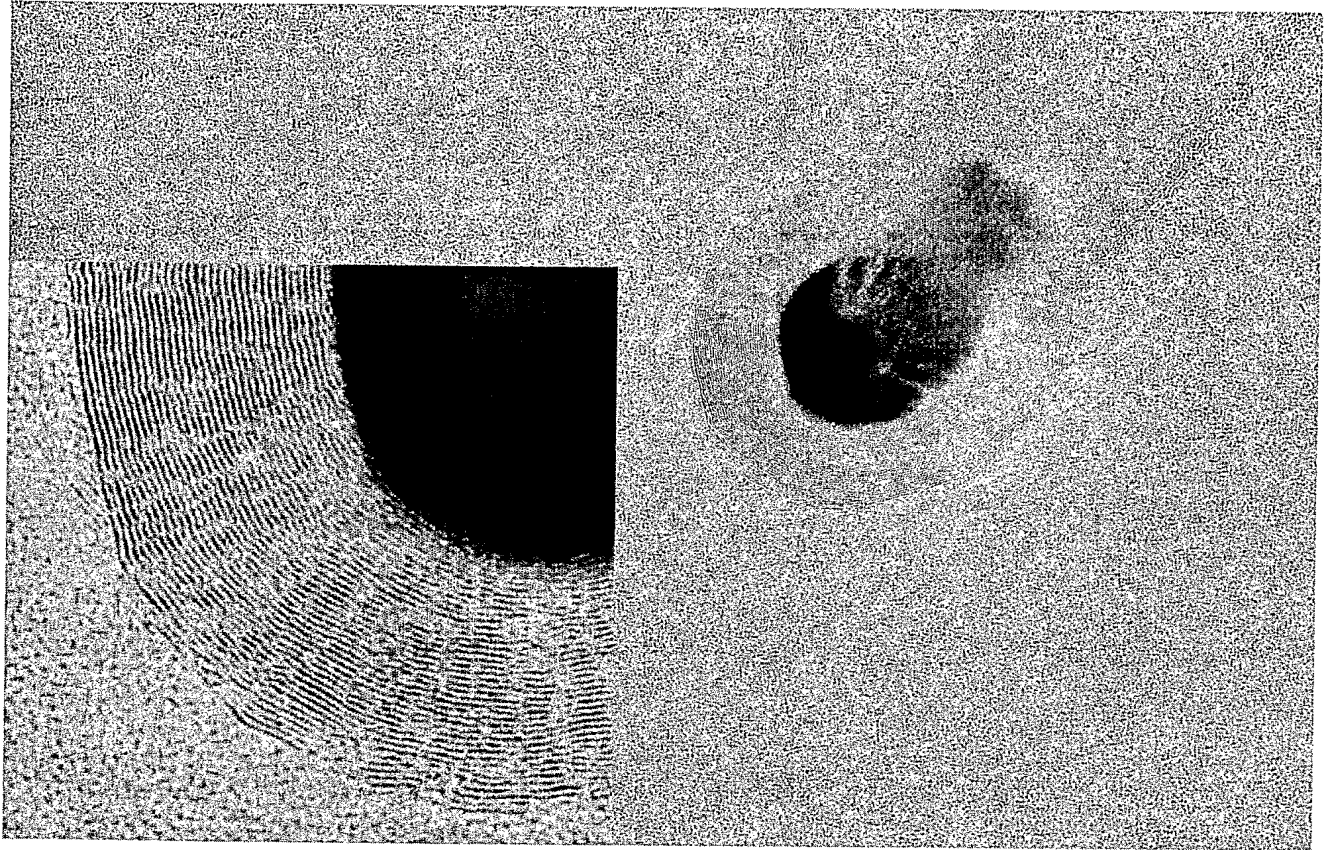


Fig. 1



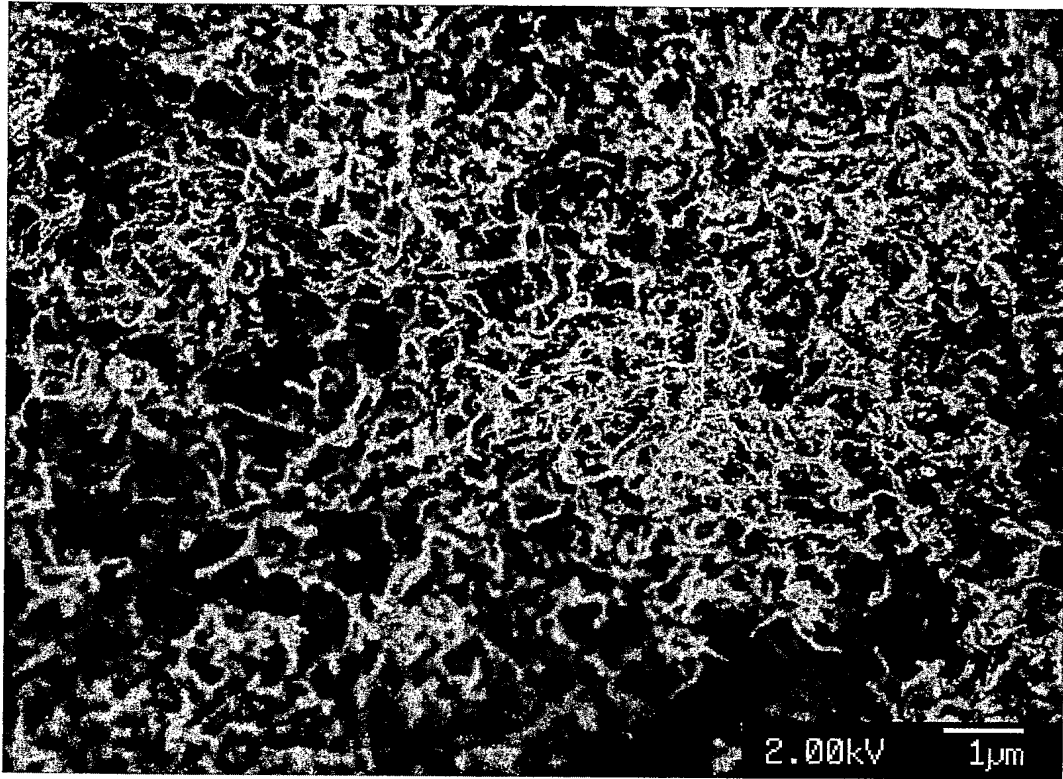


Fig. 2





Fig. 3



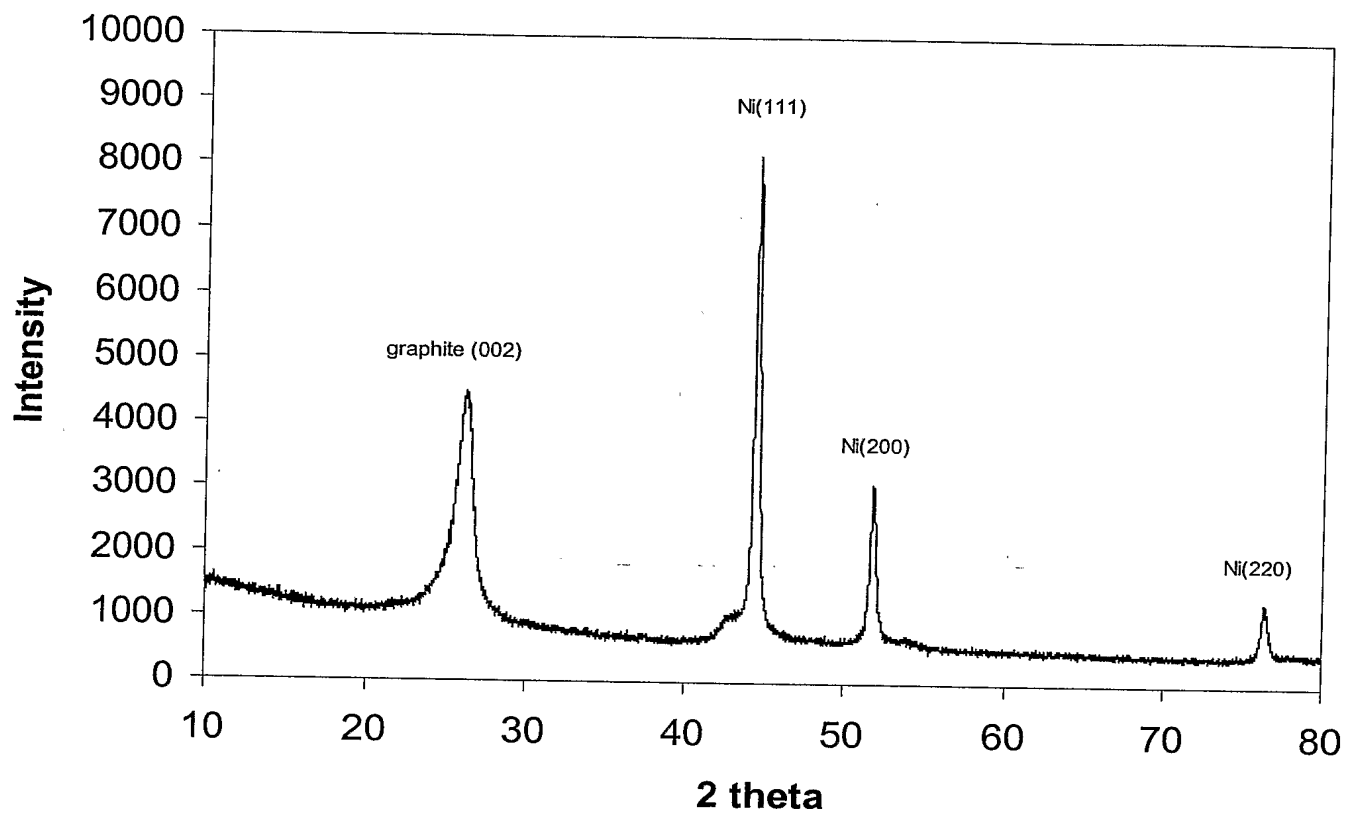


Fig. 4



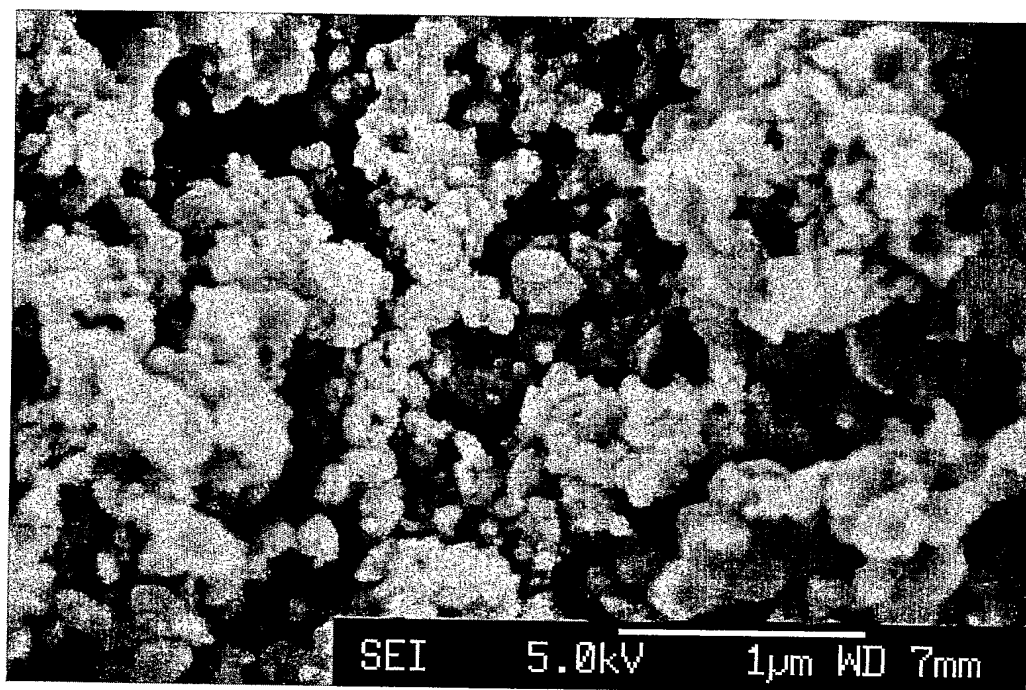


Fig. 5



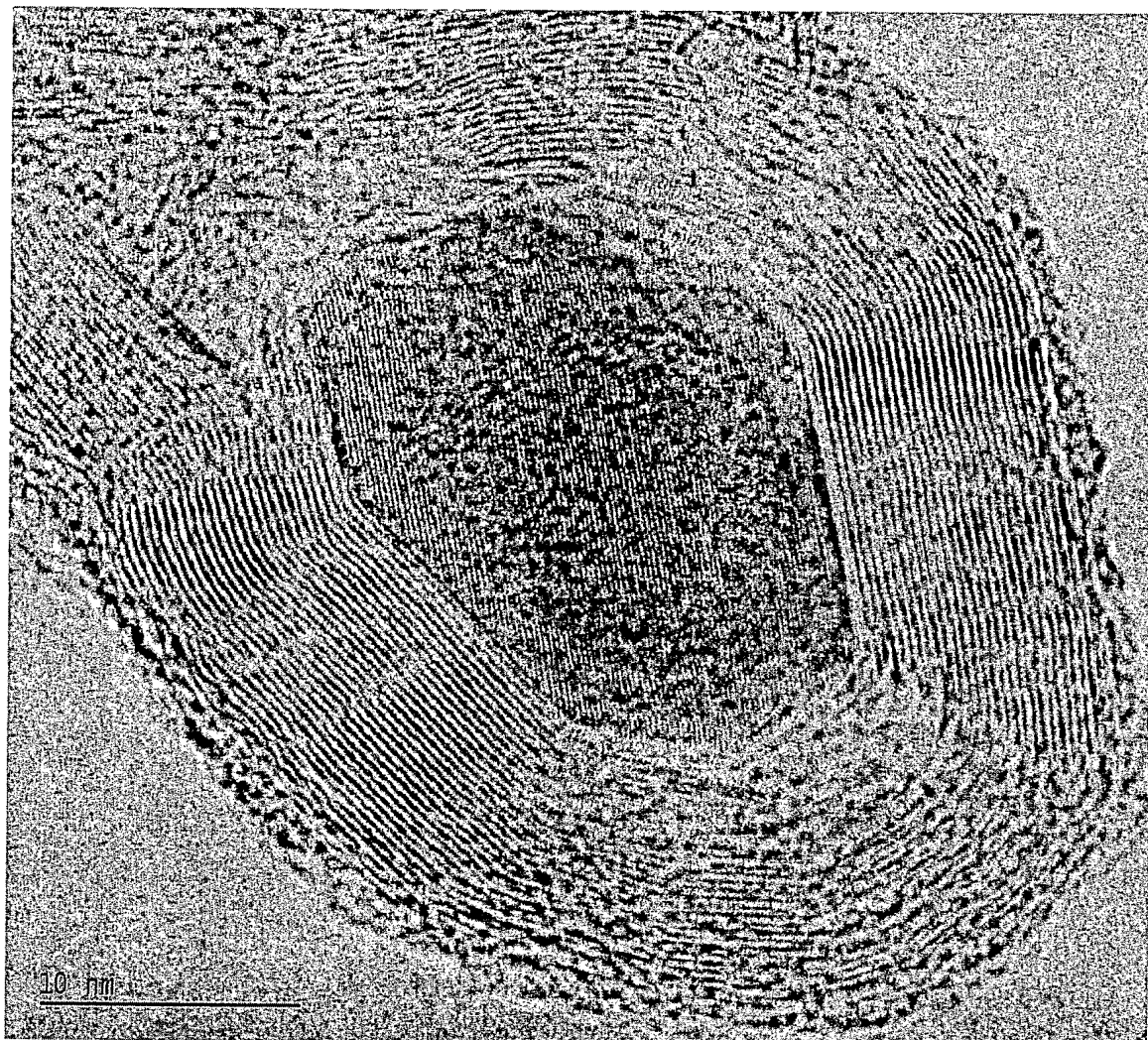
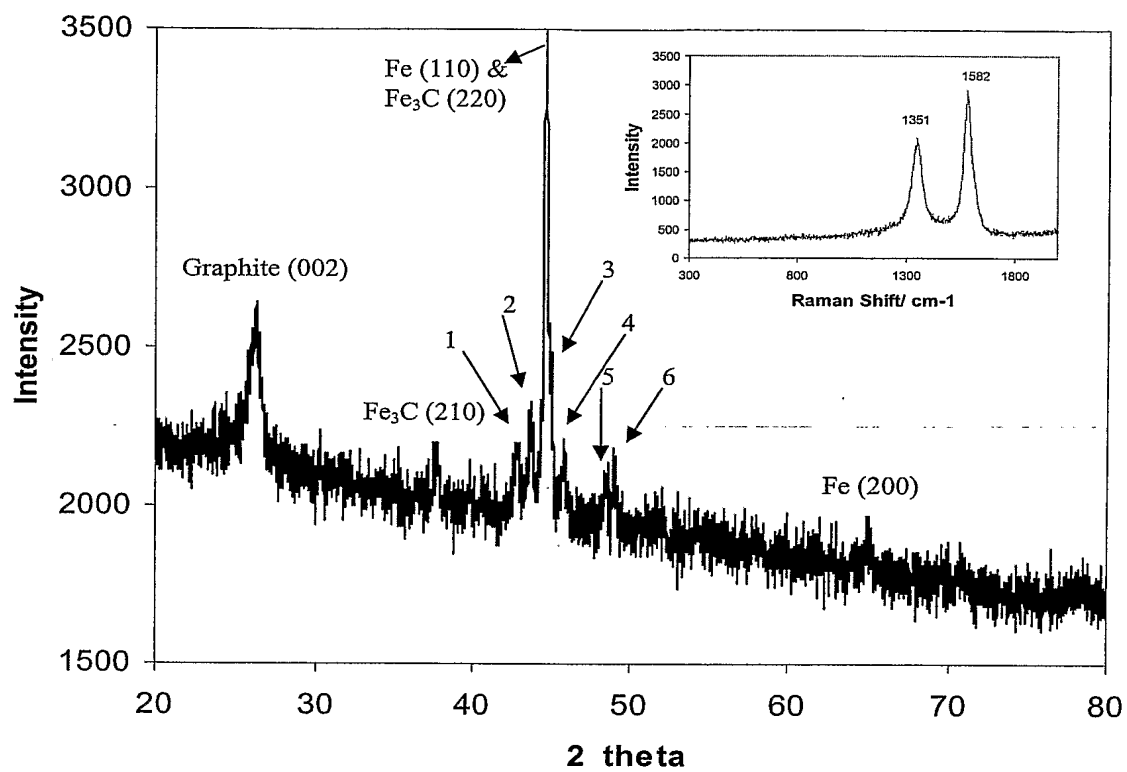


Fig. 6





1: Fe₃C (211); 2: Fe₃C (102); 3: Fe₃C (031); 4: Fe₃C (112); 5: Fe₃C (131);
6: Fe₃C (221);

Fig. 7

